

COMPUTATIONAL MECHANICS MODELLING OF CARBON NANOTUBE–
BASED NANOCOMPOSITES

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*To all my beloved family members;
my adorable parents, my lovely husband,
my kind sisters
and
to the new sweet member of my family, Ava.*

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ABSTRACT

Composites are engineered materials that consist of two or more insoluble phases combined together; a continuous phase, known as the matrix, as well as interdispersed component known as the reinforcing phases. If at least one of the constituent phases of a composite material is less than 100 nm in size, e.g. the reinforcing phase, this composite is commonly termed nanocomposite. Among all the variety of different fillers that can be used as a nanocomposite's reinforcing phase, carbon nanotubes (CNTs), have shown to be promising candidates for their very specific and remarkable mechanical and physical properties. Carbon nanotube-based nanocomposites, i.e. composite materials in which carbon nanotubes are used as the composite's reinforcing phase, are therefore very much interesting for scientists and scholars, for the many outstanding applications that they can contribute to the world of science and industry. This study uses a computational mechanics approach to numerically characterise the properties of single- and multi-walled carbon nanotubes by simulating their molecular structure, by the finite element method, at the first stage. Special emphasis is given to investigate the effect of some imperfections in the structure of both single- and multi-walled CNTs on their mechanical properties, namely perturbation, missing atoms and silicon doping in the structure of CNTs. Later on, a unit cell of a composite material, consisting of a single CNT and its surrounding matrix is simulated and studied and finally, parallel CNTs, as reinforcement fibres in a macroscopic polymer matrix, are randomly distributed and modelled to obtain the mechanical properties of the structure and observe how random distribution of short fibres influences the properties of nanocomposites. Based on the results of this research, any type of imperfection in the structure of carbon nanotubes and carbon nanotube-based nanocomposites leads to a Young's modulus value of less than 1TPa.

ABSTRAK

Komposit adalah bahan kejuruteraan yang terdiri daripada dua atau lebih fasa tidak larut yang digabungkan bersama-sama; fasa sejajar, yang dikenali sebagai matriks, serta komponen tersebar-dalam yang dikenali sebagai fasa pengukuh. Jika sekurang-kurangnya satu fasa unsur bahan komposit adalah kurang daripada 100nm dalam saiz, contohnya bagi fasa pengukuh, komposit ini biasanya diistilahkan sebagai nanokomposit. Di kalangan semua pelbagai bahan pengisi yang berbeza yang boleh digunakan sebagai fasa pengukuh, nanotub karbon (carbon nanotubes – CNTs), telah menunjukkan kebolehnya untuk menjadi calon terbaik yang sangat khusus dan luar biasa dari sifat mekanikal dan fizikalnya. Nanokomposit berasaskan nanotub karbon, iaitu bahan komposit di mana nanotub karbon digunakan sebagai fasa pengukuh komposit, adalah sangat menarik untuk digunakan oleh ahli-ahli sains dan cendekiawan, bagi banyak aplikasi yang boleh disumbangkan kepada dunia sains dan juga industri. Fokus utama kajian ini adalah untuk mencirikan sifat-sifat nanotub karbon berdinding tunggal dan berdinding pelbagai dengan membuat simulasi struktur molekul mereka menggunakan kaedah unsur terhingga, pada peringkat pertama. Tumpuan khusus akan diberi untuk mengkaji kesan ketidaksempurnaan dalam struktur kedua-dua CNTs berdinding tunggal dan berdinding pelbagai ke atas sifat mekanikal mereka. Kemudian, sel unit bahan komposit yang terdiri daripada CNT tunggal dan matriks sekitarnya akan disimulasi dan dikaji dan akhirnya CNTs sebagai pengisi tetulang dalam matriks polimer makroskopik akan dimodelkan dan dikaji untuk mendapatkan sifat-sifat mekanik struktur. Berdasarkan keputusan kajian ini, apa-apa jenis ketidaksempurnaan dalam struktur nanotub karbon dan nanokomposit berasaskan karbon nanotub akan mengakibatkan nilai modulus Young kurang daripada 1TPa.

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LIST OF ABBREVIATIONS

FEM	–	Finite element method
MD	–	Molecular dynamics
CNT	–	Carbon nanotube
SWCNT	–	Single-walled carbon nanotube
DWCNT	–	Double-walled carbon nanotube
MWCNT	–	Multi-walled carbon nanotubes
TEM	–	Transmission electron microscope
RM	–	Rule of mixture
HDPE	–	High density polyethylene
BEM	–	Boundary element method
RVE	–	Representative volume element
ERM	–	Effective reinforcing modulus
nano-Al	–	Nanocrystalline-aluminium
UHMWPE	–	Ultrahigh molecular weight polyethylene
PET	–	Poly ethylene terephthalate

LIST OF SYMBOLS

\vec{C}_h	—	Chiral vector
θ	—	Chiral angle
a_0	—	Length of each unit vector
b	—	Carbon–carbon bond length
R	—	Radius
D, d	—	Diameter
t	—	Thickness
r	—	Distance
L	—	Length
A	—	Area
\bar{m}	—	Mass density
V_{LJ}	—	Lennard–Jones potential
F_{LJ}	—	Lennard–Jones force
σ	—	Stress
ε	—	Strain
F	—	Force
T	—	Torque
P_{cr}	—	Critical load
f	—	Resonance frequency
E	—	Young’s modulus
G	—	Shear modulus
ν	—	Poisson’s ratio
V_{CNT}	—	Volume fraction of CNTs
U	—	Strain energy
P	—	Pure axial load

M	—	Pure bending moment
T	—	Pure twisting moment
I	—	Second moment of area
J	—	Polar moment
Δb , $\Delta\alpha$ and $\Delta\beta$	—	Tensile, bending and twist angle deformations
η_L	—	Length efficiency factor
η_o	—	Orientation efficiency factor
k_r , k_θ and k_φ	—	Molecular mechanics force constants
k	—	Spring constant
K	—	Effective length constant

CHAPTER 1

INTRODUCTION

Composites are engineered materials that consist of two or more insoluble phases combined together; a continuous phase, known as *the matrix*, as well as interdispersed components known as the *reinforcing phase*. The matrix is typically the major constituent that provides durability for the overall composite and it can be for instance, a metallic, a ceramic or a polymer material. The reinforcing inclusions are the structure's load carriers that can be in the form of fibres, particles, or flakes. This phase of the composite structure provides its stiffness and strength. Now if at least one of the constituent phases of a composite material is less than 100 nm in size, e.g. the reinforcing phase, this composite is commonly termed *nanocomposite*.

1.1 Composite structure

The reinforcing phase and matrix are the major constituents in all reinforced polymer composites. Therefore, suitable selection of type, amount and orientation of these components is very important and has a significant effect on the characteristics of the produced composite; such as its tensile and compressive strengths, fatigue

strength and failure mechanisms, electrical and thermal conductivities, specific gravity, and cost (Kaw, 2006).

1.1.1 Reinforcing phase types

Fibres can be classified as follows:

(a) Glass fibres

Glass fibres are usually isotropic and as a result of their low cost, high chemical resistance, excellent insulating properties and high tensile strength, they are the most common reinforcing materials for polymeric matrix composites. However, they have some disadvantages such as low tensile modulus, relatively high specific gravity, low fatigue resistance, high hardness and sensitivity to abrasion that decrease their tensile strength. The two most important kinds of glass fibres are called *E-glass* fibres, named because of their high electrical properties, and *S-glass* fibres, named so because of their high tensile strength (Kaw, 2006).

(b) Aramid fibres

These types of fibres are anisotropic and the most widely used *organic* fibres. Tensile strength, stiffness, and toughness of them are very high in the axial direction of the fibre. However, their tensile strength and stiffness in the transverse direction is relatively low. Low compressive strength is the major disadvantage of these types of reinforcing fibres.

(c) Boron fibres

Boron fibres are one of the first high performance fibres available for use as reinforcing phase in composite materials. The diameter of boron fibres is in the

range of 0.1–0.2 mm, which is an order of magnitude larger than glass, aramids, or graphite fibres. But their large diameter and high stiffness restricts their bend radius greatly, offering high resistance to buckling, which in turn contribute to an excellent compressive performance of boron–reinforced composites.

(d) Ceramic fibres

Some examples of ceramic fibres are *silicon carbide* and *aluminium–boron–silica* fibres. An outstanding feature offered by ceramic fibres is their resistance to extremely high temperatures, while still maintaining competitive structural properties. Having applications in metal and ceramic matrix composites, ceramic fibres are suitable options for reinforcing metal matrices in which boron and carbon fibres exhibit adverse reactivities.

(e) Graphite and carbon fibres

The terms *graphite* and *carbon* are often interchangeably used in the composite community. Major advantages of carbon fibres are their extraordinarily high tensile strength–weight ratios, as well as tensile modulus–weight ratios, very low coefficient of thermal expansion and high fatigue strengths. They behave anisotropic and have a high longitudinal stiffness due to alignment of the basal planes parallel to the fibre axis. Their low impact resistance and high cost are their major disadvantages, but these reinforcing materials are mostly very appropriate options in aerospace industry, where weight savings is considered to be more critical than lowering costs.

Transferring stresses between the fibres and protect the surface of the fibres from mechanical abrasion are the main role of the matrix in a fibre–reinforced composite. The matrix provides lateral support against the possibility of fibre buckling under compression loading (Kaw, 2006).

1.1.2 Matrix phase types

Matrices can be classified as follows:

(a) Polymeric matrix

Polymer is defined as a long chain of molecules, containing one or more repeating units of atoms joined together by strong covalent bonds. Polymeric materials are collections of a large number of polymer molecules of similar chemical structure, but not necessarily of equal length. In solid state, these molecules are either frozen in space in a random fashion, e.g. for amorphous polymers, or in a mixture of random and orderly folded fashions, e.g. for semi-crystalline polymers.

Among different types of polymeric matrices, thermoplastic and thermoset polymer matrices are two major categories. In thermoplastic polymers, individual molecules are linear in structure, without any chemical linking between them. Thermoset polymers, on the other hand, consist of molecules which are chemically joined together by cross-links, forming a rigid three-dimensional network structure during polymerization reaction which as a result, cannot be easily melted or reshaped under heat and pressure.

(b) Metal matrix

Metals have high modulus and yield strength which candidate them for applications requiring high transverse strength and compressive strength. Another important advantage of a metal matrix, over the polymeric matrix, is its long-term resistance to severe environmental conditions, such as being used in high temperatures, or enduring a variety of mechanical and thermal treatments, allowing them to be plastically deformed and strengthened.

Metals have some disadvantages as well, such as high specific weight, high melting points and hence hard to process. They also have the tendency toward corrosion at the matrix/fibre interface (Kaw, 2006).

1.1.3 Carbon nanotube–based composites

Among all the variety of different fillers that can be used as a nanocomposite's reinforcing phase, *carbon nanotubes* (CNTs), have shown to be promising candidates for their very specific mechanical and physical properties which will be explained later. carbon nanotube–based nanocomposites, i.e. composite materials in which carbon nanotubes are used as the composite's reinforcing phase, are therefore very much interesting for scientists and scholars, for the many outstanding and remarkable applications that they can contribute to the world of science and industry. They are expected to influence many fields in terms of technology and industry. They will have applications in many diverse fields such as energy, signal processing, medicine, biotechnology, information technology, aerospace, agriculture, and environment (Wang *et al.*, 2010). These outstanding materials can be used as stand-alone nanomaterials or as reinforcements in composites for a wide variety of application. Therefore, several detailed studies have been conducted to explore different properties of carbon nanotubes and carbon nanotube based composite materials.

Composite materials mostly show more significant advantageous properties compared to monolithic materials. Monolithic metals and their alloys cannot always meet the demands of today's advanced technologies and performance requirements. It means that by incorporating reinforcements into a, for instance, metallic, ceramic or polymer matrix, the properties of the matrix improves to a higher mechanical strength, more significant temperature stability and better chemical durability. The

existence of reinforcing elements improves the structure's physical and chemical properties.

The main focus of the project is therefore to characterise the properties of single- and multi-walled carbon nanotubes by simulating their molecular structure using the *finite element method* (FEM), at the first stage. Special emphasis will be given to investigate the effect of *imperfections* in the structure of both single- and multi-walled CNTs on their mechanical properties. Later on, a unit cell of a composite material consisting of a single CNT and its surrounding matrix will be simulated and studied and finally CNTs as reinforcement fillers in a macroscopic polymer matrix will be modelled and studied to obtain the mechanical properties of the structure.

1.2 Statement of problem

There are very vast variety of emerging applications for CNTs and CNT-based polymer nanocomposites, ranging from nano-electronics to biomedical devices. Due to the restrictions in manufacturing perfect CNTs, different configurations of defects in CNTs should be investigated before proceeding to the high cost of making them experimentally available; namely, *vacancies* i.e. single or several carbon atoms being missed in the related C-C bonds and therefore in the whole structure, improper location of carbon atoms making the structure *perturbed*, as well as the existence of other atoms *doped* in the structure that will all influence the properties of nanostructure material.

Finding out *how defects and imperfections influence the mechanical properties of different types of CNTs and CNT-based polymer nanocomposites*, before getting involved in the burden of experimental production and its pertinent

high expenses is the main issue that this investigation tries to study as much as possible. It is quite necessary and helpful to study how these defects and imperfections influence the mechanical properties of different types of CNTs and to embed them later in a polymer matrix and study the properties of the nanocomposite for its potential applications ranging from nanoelectronics to biomedical devices.

1.3 Scopes of the study

(a) To characterise the properties of single- and multi-walled carbon nanotubes by simulating their molecular structure using the finite element method.

(b) To model and study the composite material consisting of CNTs as reinforcement fillers inside a polymer matrix.

(c) Special emphasis will be given to investigate the effect of imperfections in the structure of both single- and multi-walled CNTs as nanocomposites' reinforcement elements independently, as well as the randomness of the distribution of fibres inside matrix, on the mechanical and physical properties of the whole structure by means of the finite element method.

1.4 Research objectives

The objectives of this research can be stated as follows:

(a) To determine the effects of deficiencies and imperfections in carbon nanotube's structure on its main mechanical properties.

(b) To simulate the structure of a unit cells of CNT/polymer matrix nanostructure as a basic investigation for evaluating the macroscopic structure later.

(c) To simulate the macroscopic structure of different CNT/polymer matrices and study their mechanical and physical properties with different orientations and dispersion densities.

1.5 Structure of the thesis

This dissertation is organised in five chapters as follows:

Chapter 1, the current chapter, looks mainly on the significance of the research topic and gives a general definition of nanocomposites and carbon nanotube-based composites. The scopes and objectives of the research are also presented in this chapter.

Chapter 2 is arranged to introduce the basic definitions pertaining to the involved nanomaterials and to give a brief review of the main steps forward in the path of characterising the above-mentioned nanostructures.

The methods applied and the steps taken for investigating the structures' properties and achieving the appropriate results are presented in *Chapter 3*, whereas the obtained results are depicted and discussed in detail in *Chapter 4*.

Finally, a conclusion of the whole research approach and the achieved results is introduced in *Chapter 5*.

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